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A New System of Cement Testing.

By C. R. PLATZMANN.

THE December 1934 number of CEMENT AND CEMENT MANUFACTURE contained an article dealing with the question of an international specification for cement, and with the attendant difficulties. From the tables of specifications of various countries published in your January number it appears that little progress has been made towards this goal. One reason for this is that many small States treat the question as a national one, instead of adopting one of the more important specifications which are known to ensure a cement of high quality. From this point of view the tables are found to contain no fewer than fifteen superfluous specifications. The remainder fall into two groups, based on the English and German specifications respectively. The basic difference between these is the use of a mechanical method of tamping the test-pieces in the German standard. This divergence is a serious obstacle to the adoption of a common standard, although recently opinion in England has inclined towards the mechanical preparation of test-pieces and the inclusion of compression tests. Even assuming that agreement were possible, however, it would seem that the entire system of specification is due to undergo a fundamental change from the present physical-mechanical basis to a foundation on chemical constitution.

Before considering this, some of the arguments against the present system may be mentioned. While the manufacturer regards standard tests in relation to works control, the user views them as a criterion of the practical value of cement, and a compromise can satisfy neither. The user is not helped by results which apply to conditions of consistency, etc., which are very different from those of practice. The increase of crushing strength and the change in the relation between crushing and tensile strengths tend towards cement liable to expansion. The test on the 170-mesh per inch sieve is no criterion of fineness. The active fraction of a cement can only be evaluated by means of an apparatus such as the elutriator used by the Associated Portland Cement Manufacturers, Ltd.

A further point is the increasing use of special cements for which the ordinary specifications are inadequate. Thus there is no ready means of determining contraction, which is of importance in connection with concrete roads and cast stone. When large masses of concrete are involved the heat of hydration is important. For such reasons there have recently been recommendations for a system comprising a series of cements. Moncrieff suggests three grades of ordinary Portland cement. Kühl proposes classifying cements according to their use, e.g., a cement of high crushing strength for reinforced concrete work, one of high initial strength for road construction, one of low heat of hydration for use in large masses of concrete, and one of low contraction for cast stone. Kühl's proposals are allied to the question of adopting a system of specification based on chemical constitution.

It is only recently that the constitution of Portland cement has been definitely settled by means of X-ray analysis, and it may be definitely accepted that the chief constituents are tricalcium silicate, $3CaO.SiO_2$, beta dicalcium silicate, $2CaO.SiO_2$, tricalcium aluminate, $3CaO.Al_2O_3$, and the compound $4CaO.Al_2O_3.Fe_2O_3$. From the work of the United States Bureau of Standards, particularly of Bogue and Lerch, we know that the proportions of these constituents can be calculated from the oxide analysis. The functions of the several compounds are also known. Thus high $3CaO.SiO_2$ content gives high crushing strength, the slower hydrating $\beta 2CaO.SiO_2$ gives good long-period hardening properties, and $3CaO.Al_2O_3$, with its vigorous reaction and high heat of hydration, accelerates initial hardening through copious crystal formation, although it can also cause contraction exceeding 7 per cent. From the constitution, as calculated from the oxide analysis, the properties of a cement can be determined with considerable certainty. It might be argued that such calculations do not indicate the extent to which the lime is combined, but there are to-day adequate methods of determining the free lime in cement. Further, the heats of solution and of hydration of the individual constituents of cement can be determined by a method published by Bogue and Lerch in the *Bureau of Standards Journal of Research* for 1934. It is therefore now possible to place this chemical method of evaluating cement on a practical basis with a view to a new type of standard specification.

Once this basic principle is admitted, the attainment of international agreement will offer much less difficulty than on the present physical-mechanical system. Setting time, soundness, and strength tests can of course be retained, although these properties would be ultimately determined by the constitutional composition. If, for example, definite compositions be laid down for the cements suggested by Kühl, with a limited heat of hydration (i.e., a limited $3CaO.Al_2O_3$ content) for the cement to be used for large masses of concrete, the standard specifications are only a consequence of the basic principle of chemical composition.

In view of the tendency towards a radical change in the standards it is not too much to hope for the early realisation of these proposals, which offer both an excellent basis of specification and the possibility of a gradual approach to international agreement.

The Setting Time of Portland Cement.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

(*Concluded from page 55.*)

Influence of Calcium Sulphate.

In one form or another this substance is universally used for retarding the setting time of Portland cement, and its action has therefore been more extensively studied. Gypsum, being the cheapest form of calcium sulphate, is most commonly employed, although plaster of Paris is also used by a few manufacturers. At one time it was considered that the added gypsum must be converted into plaster of Paris in order to be effective, and that this was brought about by the heat of the mill. It is common knowledge, however, that finely-ground gypsum added to fully ground clinker produces slow-setting cement. It is possible, though doubtful, that in this case the gypsum is dehydrated by the cement in the dry state merely by mixing, due to the strong affinity of cement for water. According to W. Davis[29] gypsum begins to lose its water of crystallisation at 208 deg. F., and a large part of its water may be driven off at 225 deg. F., but under some conditions gypsum begins to lose its water at 104 deg. F. In a modern tube mill the temperature usually ranges from 230 to 270 deg. F. In addition, there is the pressure caused by the weight of the charge. Hence under cement grinding conditions it is likely that gypsum can lose a proportion of its water of crystallisation and that this is absorbed by the cement as fast as it is liberated, tending to hydrate a portion of the cement. On the other hand, the power of clinker to absorb water during grinding is limited. Addition of calcium sulphate improves very materially both the plasticity and strength of cement, and there is a certain optimum sulphur trioxide content at which these improvements are at a maximum. The rate of set of cement cannot easily be graded to any fixed time by varying the amount of gypsum added. Generally, additions of successively increasing proportions of gypsum to clinker have little effect in the case of quick-setting cement until a certain proportion is reached, and then the cement suddenly changes from quick to slow setting. In this connection the paper by Witt and Reyes [17] is interesting. In general, it may be said that 3.5 to 4.7 per cent. gypsum produces a maximum retardation of set. Above about 5.3 per cent. gypsum accelerates the set. When the gypsum content becomes very excessive (about 15 per cent.) the set is again retarded.

Many workers have proved that the various forms of calcium sulphate all have a retarding effect on the set of Portland cement. Plaster of Paris ($2CaSO_4.H_2O$) is said to be a more efficient retarder than gypsum ($CaSO_4.2H_2O$), which is more efficient than anhydrous calcium sulphate or anhydrite ($CaSO_4$). This is supported by Tippmann[18] who found that plaster is twice as efficient as gypsum and that anhydrite is the least efficient. He said that the effects of the three types of calcium sulphate in raising the strength of the cement were similar to their effects on the setting time, i.e., anhydrite was the least efficient. The difference in efficiency of the modifications of calcium sulphate is said by many observers

to be due to differences in two of their physical characteristics, namely, solubility and hardness. Bamber [19] pointed out that inasmuch as the effect of calcium sulphate in retarding the initial set of cement depends upon the rapidity of solubility in the period immediately after the addition of water, and the quantity that can quickly be brought into solution, it follows that the form of calcium sulphate having the greatest solubility will be the most effective. Figures are given for the quantities of the various forms of calcium sulphate which dissolve in 100 cc. water at 60 deg. F. during different periods of time. Taking the five-minute figure for dead-burned plaster ($CaSO_4$) as 1.0, we have

	Relative quantity dissolved in five minutes.
$2(CaSO_4).H_2O$, plaster of Paris	4.4
$CaSO_4.2H_2O$, gypsum	1.2
$CaSO_4$, dead-burned plaster	1.0

These figures indicate that plaster produces the same effect as 3.5 times the quantity of gypsum ; this is important in view of the known defects which may be produced by the excessive addition of gypsum to cement, especially if the cement is to be placed under sea-water before setting commences. The conclusions of W. P. Gano[20] support Bamber's conclusions, for they show that plaster is about 2.5 times as efficient as gypsum and that dead-burned plaster is not so efficient as gypsum. Meade[9] points out that the action of the forms of calcium sulphate depends on the fineness to which they are ground and possibly on the thoroughness with which they are mixed with the cement. The fineness to which the retarder is ground increases the surface exposed and this materially affects the rate of solution. That plaster of Paris has a greater effect as a retarder than other forms of calcium sulphate is explained by the fact that it is not only about four times as soluble as gypsum but it is also softer and if ground with the cement would be reduced to a much finer condition. Similarly gypsum is a little more soluble and much softer than dead-burned plaster. This accounts for the fact that cement retarded with anhydrite has a lower plasticity, and also for Berger's observation that a higher sulphur trioxide content is required than with gypsum to produce the same retardation of the set. Platzmann[21] stresses the observation that the efficiency of gypsum retarder depends largely on its solubility.

Theories of the Retardation of Set of Cement by Admixture of Foreign Salts.

Chemical Theories.

Jordis[23] considered that the action of salts affecting setting time is chemical and that they react with the cement. Thus ammonium salts mixed with cement, even in the dry state, undergo decomposition with evolution of ammonia[24]. Ferric sulphate mixed with cement undergoes some decomposition with formation of ferric oxide[2].

Forsen[25] put forward a remarkable theory of the chemical action of retarders. His conclusions are :—

(1) The rapid setting of pure ground clinker alone depends on the hydrolysis

of the unstable tricalcium aluminate according to the equation

$$3CAO.Al_2O_3 + 6HOH = 3Ca(OH)_2 + 2Al(OH)_3$$

(2) The slow setting due to the action of retarders is caused by the formation of complex compounds which form spherolithic crystals according to the equation

$$3CaO.Al_2O_3 + CaX_2 + 10H_2O \rightarrow 2\left\{\left[Al\begin{pmatrix}HO\\HO\end{pmatrix}Ca\right)_2(H_2O)_2\right](OH)_2X\right\}$$

The formation of the complex compounds prevents the hydrolysis of the tricalcium aluminate, and the slowing of the speed of reaction depends on the reduced solubility of tricalcium aluminate in solutions of lime salts.

(3) On the addition of greater quantities of the retarder spherolithic crystals form in great quantity and now, according to Forsen, the set is accelerated instead of retarded.

(4) Still stronger concentrations of this type of retarder lead to a form of unsoundness similar to gypsum expansion. This is due to the conversion of tetrahydroxy complexes into hexahydroxy compounds, thus

$$2\left\{\left[Al\begin{pmatrix}HO\\HO\end{pmatrix}Ca\right)_2(H_2O)_2\right](OH)_3\right\} + 3CaX_2 \rightarrow 2\left\{\left[Al\begin{pmatrix}HO\\HO\end{pmatrix}Ca\right)_3X_3\right\} + 4H_2O + Ca(OH)_2$$

(5) Lime expansion depends on the formation of readily soluble calcium hexahydroxy-aluminium hydroxide complex compounds as follows:

$$\left[Al\begin{pmatrix}HO\\HO\end{pmatrix}Ca\right)_2(H_2O)_2\right](OH)_3 + Ca(OH)_2 \rightarrow \left[Al\begin{pmatrix}HO\\HO\end{pmatrix}Ca\right)_3\right](OH)_3 + 2H_2O.$$

The view has often been put forward that the retardation of the set of cement by gypsum addition is due to the formation of calcium sulphoaluminate. Klein and Phillips opposed this on the following grounds: (1) The quantity of sulphoaluminate formed steadily increases from the beginning to the end of the initial set; (2) Increasing the gypsum increases the amount of sulphoaluminate formed, although the set may be quickened by increasing gypsum concentration; (3) The formation of this compound is only incidental to the initial set and not the cause of its retardation, since the compound is formed before, during, and after the set.

Physical Theories.

There are two difficulties in the way of chemical theories of retardation of the set of cement by addition of foreign substances, namely: (1) The effect of many of the substances depends on the percentage present, i.e., additions below a certain amount may produce a certain effect whilst a greater quantity will produce the opposite effect; (2) the large number of substances of widely different chemical natures which are effective, for example, calcium chloride, potassium dichromate, borax, sugar, etc.

Rohland[22] was one of the first to draw attention to the properties of salts in modifying setting time; he considered the action to be due to a change of the

solubility of the substance undergoing hydration. At a later date when reviewing previous work Rohland stated that variations in setting times of cements mixed with various concentrations of different salt solutions are not due to the presence of free calcium oxide but to the formation of absorption products. These products are formed from the salt solution and the colloidal material resulting on mixing cement with water and their presence hinders or accelerates the coagulation of the colloid with subsequent variation in the setting time.

Reibling[26] held the theory that as plaster dissolves it ionises and reduces the solubility of the other calcium ions already present, causing lime to be less readily dissolved, hydration to take place more slowly, and setting time to be retarded. If this were so increasing amounts of plaster should give a correspondingly slower set. This is not true of Portland cement, however. In the thinning of clay slips, very small quantities of an electrolyte are added. At definite concentrations of electrolyte in the slip there are points of maximum and minimum viscosity, and by increasing or decreasing the concentration of electrolytes complete coagulation may result.

McKenna[27] pointed out that the amorphous material in setting cement separates in at least two stages, normal cements showing a relaxation of the first stiffening at about the third hour, followed by a resumption of the hardening. The explanation given is that the break indicates the separation of a compound from supersaturated solution and softening of the amorphous mass by the water liberated. Later, by absorption of water, hardening proceeds. Bleininger likewise stated that the electrical conductivity of a paste of cement and water increases rapidly at the time of initial set, which is in favour of a supersaturation theory. The problem in initial set is therefore probably one involving the action of small amounts of electrolytes in retarding the coagulation of the amorphous material. This theory is supported by the fact that aluminates coagulate and separate as amorphous bodies from supersaturated solutions, the rate of coagulation being affected by the electrolyte concentration. Thus, with a certain and definite concentration of gypsum, maximum hydration is obtained and at the same time the rate of coagulation is retarded thereby lengthening the setting time.

The time of set and the causes of its variation have been dealt with by Phillips.[28] He considered that the setting of Portland cement is essentially a colloidal process, and it therefore follows that the time of set will materially depend on the rates of dispersion and coagulation of the colloid. Chemical composition of the cement determines the percentage and the nature of the ingredients (i.e., silicates and aluminates) composing it. Bearing in mind the chemical composition and fineness factors, it may be said (1) that the rate of dispersion of an ingredient to the gel state is influenced by its previous aeration, the amount of water used in gauging, the amount of heat developed during hydration, the adsorption of positive ions, the valency of the ions, and the amount of the dissociation of the salts furnishing those ions, and (2) that the rate of coagulation is affected by the amount of dispersion, the syneresis of the gel, the neutralisation of previously adsorbed positive ions by negative ions, the ad-

sorption of undissociated salt and, when gypsum is added, by the fineness and set of the plaster itself. Such an explanation indicates how electrolytes can affect the setting time of cement.

Tricalcium aluminate is a good example of adsorption, for the treatment with water changes the composition of only the outer surface of the grains (a hydrated film being formed) while the interior is unchanged ; any ionic activity will therefore be confined to the surface. It cannot be considered that no absorption takes place, for the rupture of the films by mechanical treatment or the swelling of the particles will allow the penetration of liquid to the interior. However, in ordinary circumstances the first contact of liquid with the solid particles results in the formation of a film and therefore the major effects are surface effects and are due to adsorption.

Lime water effects a greater dispersion of tricalcium aluminate than does pure water, other things being equal. There is a preferential adsorption of the positive calcium ions of lime water by hydrated aluminate. When the concentration of adsorbed ions becomes sufficiently great their charges repulse each other and the aluminate is dispersed. The aluminate has a limited capacity for the adsorption of positive ions, so, if the concentration of negative ions is sufficiently increased, at some concentration of the latter the positive charges on the aluminate will be neutralised by the adsorption of negative ions. This will result in the precipitation of the uncharged aluminate, however, as the charge is neutralised and the material coagulates ; the adsorbing surface is decreased and consequently the ions are given back to solution to exert a dispersive effect on undispersed material. For this reason the dispersive effect will constantly be countering the coagulating effect.

The multiplicity of electrolytes which can vary the setting time of cement can only be satisfactorily explained, according to Phillips,[28] by the adsorption of ions of the same kind of electrical charge, their mutual repulsion causing dispersion and the further adsorption of oppositely-charged ions to neutralise the previously-adsorbed ions, thus causing coagulation. The fact that a given concentration of certain salts will retard the set and that larger concentrations will accelerate it is explained by this theory. Retardation is due to the salt effecting a greater degree of dispersion. Acceleration occurs when the coagulative effect rises superior to the dispersive effect. Increased adsorption follows as the retarding salt is increased in fineness, so that the finer the salt the greater the effect. One must also consider the effect of ionic concentration and the rate at which this concentration is attained. Thus the rate at which the positive ions go into solution and the rate at which the necessary concentration of these ions is attained are the two chief factors in causing retardation of the set.

In comparing plaster and gypsum, the former dissolves faster and it is found in practice that less plaster than gypsum is required to produce a desired retardation. Another effect still to be considered is salt peptisation ; there is generally a retardation of the set due to salt peptisation. Thus small amounts of gypsum retard the set and increasing the gypsum concentration causes an

acceleration of set, but when the gypsum content becomes excessive the set is again retarded. This latter retardation is due to the adsorption of un-ionised salt. We are dealing with an un-ionised salt in this case because the concentration is too great to allow of any considerable dissociation taking place. We encounter then the effect resulting from the adsorption of un-ionised salt which results in a kind of dispersion known as salt peptisation.

In the beginning, with small amounts of gypsum, we start with an ion peptisation because one ion is adsorbed more rapidly than the other ; with increasing salt concentration the adsorption of the first ion ($Ca^{\cdot\cdot}$) varies but slightly with the concentration, while the adsorption of the second ion (SO_4'') continues to increase relative to the first until we get neutralisation of the first and coagulation. At the same time the adsorbed salt is tending to peptise the material so that with still greater salt concentration we should expect salt peptisation to overcome coagulation and the set to be again retarded. This salt peptisation is not confined to calcium sulphate, as a number of substances such as tannin, oxalic acid, quinoline, etc., exert a retarding effect on the final set of cements. The effect here is not due to a high concentration preventing dissociation, but because, at any concentration, these substances are but slightly dissociated, if at all.

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Notes from the Foreign Press.

A Simplified Method of Testing the Resistance of Concrete to Disintegration. By A. Pogany. *Zement*, No. 43, 1934.—The resistance of a concrete to disintegration by solutions is almost completely dependent on its density, i.e., on the condition of the micropores in the cement. A quick method of determining a relative figure for the density of a specimen has been devised in which the potential difference between two electrodes embedded in the concrete is measured.

The specimens are placed in solutions of sulphuric acid of various concentrations e.g., 1, 2, and 3 per cent. In the centre of each cube two zinc electrodes are embedded and the potential difference between them measured while the cube is immersed. At the same time the potential difference between two electrodes in the solution is measured. The figures so obtained are plotted, the potential difference on the abscissa and the sulphuric acid concentration on the ordinate. For each specimen two curves are obtained, one for the potential difference between the electrodes in the specimen and one for the potential difference between the electrodes in the solution. The area enclosed between the two curves gives a measure of the density of the concrete and therefore of its resistance to disintegration. The farther these two curves are apart the denser the concrete. The test is easily carried out.

Researches on Alite. By K. Koyanagi. *Zement*, No. 43, 1934.—Modern research has definitely proved that alite is tricalcium silicate. Iron oxide and alumina are important constituents of Portland cement because they act as fluxes and help the formation of tricalcium silicate at a comparatively low temperature. By using fluxes other than iron oxide and alumina, e.g., fluorspar or gypsum, an ideal cement consisting almost completely of alite can be prepared. A cement of this type was made and gave the following strengths : Tensile strength of 3 : 1 mortar at 3 days, 570 lb. per sq. in. ; at 7 days, 640 lb. per sq. in. ; at 28 days, 695 lb. per sq. in. ; at 180 days, 838 lb. per sq. in. Compressive strength of 3 : 1 mortar at 3 days, 9,450 lb. per sq. in. ; at 7 days, 1,037 lb. per sq. in. ; at 28 days, 1,170 lb. per sq. in. ; at 180 days, 1,375 lb. per sq. in.

Comparison of the Portland Cement Specifications of the World.

On the following pages we give the completion of the tables comparing the requirements of the Standard Specifications for Portland Cement issued in various countries. The rest of the series appeared in this Journal for January, 1935. This series of tables has been prepared by Messrs. W. Watson, B.Sc., and Q. L. Craddock, M.Sc.

TABLE V.—TENSILE AND COMPRESSION TESTS (KILOGRAMS PER SQUARE CENTIMETRE).

d = day; CS = combined storage; O = ordinary cement; HS = high strength; RH = rapid hardening; QS = quick setting; SS = slow setting; LS = low strength.

Country.	Type of cement.	Tensile strength.								Compression strength.					
		Neat cement.		3 sand : 1 cement.						3 sand : 1 cement.					
		7d	28d	1d	2d	3d	7d	28d	28d CS	1d	2d	3d	7d	28d	28d CS
Argentina	O	—	—	—	—	—	20	28	—	—	—	—	230	325	—
	RH	—	—	20	25	30	35	—	50	225	350	400	450	—	600
Australia	O	—	—	—	—	—	17.6	22.8	—	—	—	—	—	200	251
Austria	O	—	—	—	—	—	17.9	—	—	—	—	—	220	—	—
Belgium	O	—	—	—	—	18	22	27	—	—	—	200	300	400	—
	HS	—	—	—	—	22	27	30	—	—	—	300	400	500	—
	RH	—	—	20	—	27	30	32	—	220	—	400	500	575	—
Brazil	O	40	45	—	—	—	14.1	19.3	—	—	—	—	70	176	—
										Neat compression test: 7d, 246; 28d, 422.					
Canada	O	—	—	—	—	—	15.8	22.8	—	None specified.					
Chile	QS	—	—	—	—	—	10	15	—	—	—	—	100	150	—
	SS	—	—	—	—	—	12	18	—	—	—	—	120	180	—
	RH	—	—	—	—	—	25	35	—	For maritime work			170	200	—
Czecho-Slovakia	O	—	—	—	—	—	18	25	30	—	—	—	200	275	350
	HS	—	—	—	—	25	28	30	40	—	—	275	375	425	500
Denmark	O	—	—	—	—	—	20	25	30	—	—	—	320	400	450
Esthonia	O	—	—	—	—	—	14	—	—	—	—	—	141	200	250
France	QS	—	—	—	—	—	6	10	—	—	20	—	35	60	—
	SS	—	—	—	—	—	10	15	—	—	60	—	100	175	—
	RH	—	—	—	—	—	20	25	—	—	175	—	250	300	—
Germany	O	—	—	—	—	—	18	25	30	—	—	—	180	275	350
	RH	—	—	—	—	25	—	30	40	—	—	250	—	400	500
Great Britain	O	—	—	—	—	21	26.3	—	—	None specified.					
Holland	O	—	—	—	—	—	18	26	—	—	—	—	200	300	—
	RH	—	—	—	—	23	26	32	—	—	—	250	350	425	—

TABLE V.—(Continued).

TENSILE AND COMPRESSION TESTS (Kilograms per square centimetre).

d = day; CS = combined storage; O = ordinary cement; HS = high strength; RH = rapid hardening; QS = quick setting; SS = slow setting; LS = low strength.

Country.	Type of cement.	Tensile strength.								Compression strength.					
		Neat cement.		3 sand : 1 cement.						3 sand : 1 cement.					
		7d	28d	1d	2d	3d	7d	28d	28d CS	1d	2d	3d	7d	28d	28d CS
Italy	O	—	—	—	—	—	25	30	—	—	—	—	350	450	—
	RH	—	—	—	—	20	30	35	—	—	—	250	450	600	—
Jamaica	O	42	—	—	—	—	22.8	25	—	None specified.					
Japan	O	—	—	—	—	—	20	25	—	—	—	150	220	300	—
Jugo-Slavia	O	—	—	—	—	—	16	—	28	—	—	—	200	280	320
	RH	—	—	—	20	—	28	—	—	—	240	—	400	—	—
Norway	O	—	—	—	—	16	22	27	—	—	—	180	250	350	—
	RH	—	—	—	18	—	27	30	—	—	250	—	375	450	—
Poland	O	30	—	—	—	—	15	19	—	—	—	—	150	250	—
Portugal	LS	—	—	—	—	—	12	16	—	—	—	—	150	240	—
	O	—	—	—	—	—	17	21	—	—	—	—	200	300	—
	For maritime work: store 12 weeks in sea water, then 3 : 1 tensile strength = 23.									Compression = 350.					
Roumania	O	—	—	—	—	—	18	25	—	None specified.					
	RH	—	—	—	—	25	35	—	—	—	—	—	300	—	—
Russia	O	—	—	—	—	—	10	14	—	—	—	—	140	—	—
Spain	O	—	—	—	—	—	19	23.6	—	—	—	—	190	280	—
	RH	—	—	—	—	25	30	38	—	—	—	250	350	450	—
Sweden	O	—	—	—	—	—	14	20	—	—	—	—	140	200	250
Switzerland	QS	—	—	10	—	—	—	—	—	50	—	—	—	—	—
	O	—	—	—	—	—	35	45	—	—	—	—	180	275	—
	HS	—	—	—	—	40	50	60	—	—	—	250	340	420	—
United States	O	—	—	—	—	—	19.3	24.6	—	None specified.					
	RH	—	—	19.3	—	26.3	—	—	—			"	"		
Uruguay	O	—	—	—	—	—	22	—	—			"	"		

NOTE.—Combined storage consists of storing the test pieces for one day in air, followed by 21 days in water and finally 6 days in air.

(*See page* 69.)

TABLE VI.

METHOD OF PREPARING BRIQUETTES AND CUBES FOR STRENGTH TESTS (ENGLISH UNITS).

Country.	Fineness of Standard sand.		Water.	Method of moulding.	Weight of hammer (lb.).		Height of fall (in.).		Number of blows.	
	Passes.	Retained by.			Tensile.	Compression.	Tensile.	Compression	Tensile.	Compression.
Argentina	0.059 in. round hole	0.039 in. round hole	P/6 plus 4.5	Klebe hammer	4.4	7.5	9.84	19.68	120	150
Australia	400 meshes per sq. in.	900 meshes per sq. in.	P/3 to P/4	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Austria	0.0531 in. round hole	0.0305 in. round hole	Not given	Klebe hammer	4.4	7.0	10.00	20.00	120	150
Belgium	400 meshes per sq. in.	900 meshes per sq. in.	P/4	Klebe hammer	4.4	6.6	9.84	19.68	120	150
Brazil	—	—	—	—	—	—	—	—	—	—
Canada	400 meshes per sq. in.	900 meshes per sq. in.	P/3 to P/4	Hand-made	—	—	—	—	—	—
Chile	400 meshes per sq. in.	900 meshes per sq. in.	7 to 8%	Klebe hammer	4.4	6.6	9.84	19.68	120	150
Czecho-Slovakia	0.0531 in. round hole	0.0305 in. round hole	Not given	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Denmark	0.0547 in. round hole	0.0291 in. round hole	Not given	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Esthonia	0.0531 in. round hole	0.0305 in. round hole	To exude after 100 to 110 blows	Bohme hammer	4.4	4.4	9.00	9.00	150	150
France	Equal parts 0.079, 0.059, and 0.039 in. holes	Equal parts 0.059, 0.039, and 0.019 in. holes	P/5	Hand-made	—	—	—	—	—	—
Germany	0.0547 in. hole	0.0291 in. hole	8%	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Great Britain	0.0336 in. holes.	0.0236 in. holes.	P/4 plus 2.5	Hand-made	—	—	—	—	—	—

TABLE VI.—(Continued).

METHOD OF PREPARING BRIQUETTES AND CUBES FOR STRENGTH TESTS (ENGLISH UNITS).

Country.	Fineness of Standard sand.		Water.	Method of moulding.	Weight of hammer (lb.).		Height of fall (in.).		Number of blows.	
	Passes.	Retained by.			Tensile.	Compression.	Tensile.	Compression.	Tensile.	Compression.
Holland	0.0547 in. round hole	0.0291 in. round hole	8%	Bohme hammer	4.4	4 4	9.00	9.00	150	150
Italy	0.059 in.	0.039 in.	Not given	Klebe hammer	4.4	6.6	9.84	19.68	120	160
Jamaica	400 meshes per sq. in.	900 meshes per sq. in.	P/3 to P/4	Hand-made	—	—	—	—	—	—
Japan	400 meshes per sq. in.	900 meshes per sq. in.	To exude after 100–110 blows	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Jugo-Slavia	—	—	—	—	—	—	—	—	—	—
Norway	0.0547 in. hole	0.0291 in. hole	To exude after 90–110 blows	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Poland	0.0547 in. hole	0.0291 in. hole	To exude after 90–110 blows	Klebe hammer	4.4	6.6	9.84	19.68	120	150
Portugal	0.059 in. hole	0.039 in. hole	Not given	Klebe hammer	4.4	6.6	9.84	19.68	120	150
Roumania	0.0547 in. hole	0.0291 in. hole	8%	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Russia	—	—	—	—	—	—	—	—	—	—
Spain	—	—	—	—	—	—	—	—	—	—
Sweden	0.0531 in. hole	0.0305 in. hole	Normal	Bohme hammer	4.4	4.4	9.00	9.00	150	150
Switzerland	400 meshes per sq. in.	900 meshes per sq. in.	% water = $11\frac{1}{2}$–13 (QS) 11 (O & HS)	Hand-made	—	—	—	—	—	—
U.S.A.	400 meshes per sq. in.	900 meshes per sq. in.	P/6 plus 6.5	Hand-made	—	—	—	—	—	—
Uruguay	—	—	—	—	—	—	—	—	—	—

P = amount of water required for normal consistency of neat cement; QS = quick setting; O = ordinary; HS = high strength.

(*See page* 69.)

TABLE VII.
METHOD OF PREPARING BRIQUETTES AND CUBES FOR STRENGTH TESTS (METRIC UNITS).

Country.	Fineness of standard sand.		Water.	Method of moulding.	Weight of hammer (kilos).		Height of fall (cm.).		Number of blows.	
	Passes.	Retained by.			Tensile.	Compression.	Tensile.	Compression.	Tensile.	Compression.
Argentina	1.5 mm. round hole	1.0 mm. round hole	P/6 plus 4.5	Klebe hammer	2	3.4	25	50	120	150
Australia	62 meshes per sq. cm.	140 meshes per sq. cm.	P/3 to P/4	Bohme hammer	2	2	23	23	150	150
Austria	1.35 mm. round hole	0.78 mm. round hole	Not given	Klebe hammer	2	3.2	25	50	120	150
Belgium	64 meshes per sq. cm.	144 meshes per sq. cm.	P/4	Klebe hammer	2	3	25	50	120	150
Brazil	—	—	—	—	—	—	—	—	—	—
Canada	62 meshes per sq. cm.	140 meshes per sq. cm.	P/3 to P/4	Hand-made	—	—	—	—	—	—
Chile	64 meshes per sq. cm.	144 meshes per sq. cm.	7 to 8%	Klebe hammer	2	3	25	50	120	150
Czecho-Slovakia	1.35 mm. round hole	0.78 mm. round hole	Not given	Bohme hammer	2	2	23	23	150	150
Denmark	1.39 mm. round hole	0.74 mm. round hole	Not given	Bohme hammer	2	2	23	23	150	150
Esthonia	1.35 mm. round hole	0.78 mm. round hole	To exude after 100–110 blows	Bohme hammer	2	2	23	23	150	150
France	Equal parts 2.0 mm. 1.5 mm. 1.0 mm.	Equal parts 1.5 mm. 1.0 mm. 0.5 mm.	P/5	Hand-made	—	—	—	—	—	—
Germany	1.39 mm. hole	0.74 mm. hole	8%	Bohme hammer	2	2	23	23	150	150
Great Britain	0.853 mm. hole	0.599 mm. hole	P/4 plus 2.5	Hand-made	—	—	—	—	—	—

TABLE VII.—(Continued).

METHOD OF PREPARING BRIQUETTES AND CUBES FOR STRENGTH TESTS (METRIC UNITS).

Country.	Fineness of Standard sand.		Water.	Method of moulding.	Weight of hammer (kilos).		Height of fall (cm.).		Number of blows.	
	Passes.	Retained by.			Tensile.	Compression.	Tensile.	Compression.	Tensile.	Compression.
Holland	1.39 mm. hole	0.74 mm. hole	8%	Bohme hammer	2	2	23	23	150	150
Italy	1.5 mm. hole	1.0 mm. hole	Not given	Klebe hammer	2	3	25	50	120	160
Jamaica	62 meshes per sq. cm.	140 meshes per sq. cm.	P/3 to P/4	Hand-made	—	—	—	—	—	—
Japan	62 meshes per sq. cm.	140 meshes per sq. cm.	To exude after 100–110 blows	Bohme hammer	2	2	23	23	150	150
Jugo-Slavia	—	—	—	—	—	—	—	—	—	—
Norway	1.39 mm. hole	0.74 mm. hole	To exude after 90–110 blows	Bohme hammer	2	2	23	23	150	150
Poland	1.39 mm. hole	0.74 mm. hole	To exude after 90–110 blows	Klebe hammer	2	3	25	50	120	150
Portugal	1.5 mm. hole	1.0 mm. hole	Not given	Klebe hammer	2	3	25	50	120	150
Roumania	1.39 mm. hole	0.74 mm. hole	8%	Bohme hammer	2	2	23	23	150	150
Russia	—	—	—	—	—	—	—	—	—	—
Spain	—	—	—	—	—	—	—	—	—	—
Sweden	1.35 mm. hole	0.78 mm. hole	Normal	Bohme hammer	2	2	23	23	150	150
Switzerland	64 meshes per sq. cm.	144 meshes per sq. cm.	11½–13 (QS) 11 (O & HS)	Hand-made	—	—	—	—	—	—
U.S.A.	62 meshes per sq. cm.	140 meshes per sq. cm.	P/6 plus 6.5	Hand-made	—	—	—	—	—	—
Uruguay	—	—	—	—	—	—	—	—	—	—

P = amount of water required for normal consistency of neat cement; QS = quick setting; HS = high strength; O = ordinary.

(*See page* 69.)

Integral Waterproofers.

THE following notes on integral waterproofers are taken, by permission, from an article by Mr. H. M. Llewellyn, B.Sc., A.I.C., in *Chemistry and Industry* dealing generally with the waterproofing of building materials :—

The various waterproofing materials which are used in admixture with mortar and concrete may be divided into two classes, viz. : (1) materials intended to reduce the permeability of the mass, but not primarily intended to alter its rate of setting ; (2) materials which are used specifically to accelerate the setting of Portland cement.

The most obvious way to make concrete impervious to the passage of water is to reduce the void space to the minimum ; actually, by exercising due care in grading of aggregates, proportioning and mixing, and in control of the amount of gauging water and the method of placing, concrete can be made sufficiently impervious for all ordinary requirements. The conditions of ordinary practice, however, do not always allow the fullest control in all these respects, and the use of waterproofing additions is intended to remedy possible deficiencies. For renderings and jointing mortars lean mixes are often necessary in order to avoid excessive shrinkage. Usually, therefore, they are more or less permeable, but the addition of a waterproofer may considerably reduce the rate at which water is absorbed, especially when the pressure of water is only slight or intermittent. Renderings which have to withstand continuous high pressures require special treatment, which will be referred to later.

Integral waterproofers are marketed in the form of powders, pastes, or liquids. Some are simply finely-ground inert substances such as chalk or talc, intended to improve the plasticity of the mix and reduce void space. Usually, however, these powders are employed in conjunction with substances of a hydrophobic character, e.g. calcium or aluminium soaps. Liquid waterproofers frequently contain substances capable of reacting with a second solution, or with the cement to form an insoluble product. Examples of this type are solutions of alkali silicates, calcium chloride, zinc sulphate, and ordinary soap. The two former substances in concentrated solution accelerate the setting of Portland cement and are used specifically for this purpose. Another " active " addition which is sometimes used is a mixture of iron filings and ammonium chloride. Here the intention is that the iron in contact with the salt should rust and in so doing expand and fill the voids. Iron filings when used alone will not rust in the interior of the mass, and hence would be classed as an inert filler. The majority of waterproofers, however, are dependent upon definite hydrophobic properties, and include a wide variety of substances comprising metallic soaps, oils, fats, waxes, resins, rubber, and bituminous materials.

As with surface waterproofers, there appear to have been few attempts to evaluate the various types of integral waterproofer on a comparative basis ; doubtless this is due to the fact that nearly all are proprietary articles and hence usually of secret composition. Investigations at the U.S. Bureau of Standards

included fifty samples of integral waterproofers, both proprietary and otherwise. The materials were classified according to their composition under six categories. Specimens of 1 : 3 : 6 Portland cement concrete prepared both with and without the waterproofing additions were tested for permeability (under a pressure of 20lb. per square inch), absorption (on immersion), and compressive strength.

In these tests it was found that calcium chloride had little effect on either permeability or absorption, but increased the compressive strength. The use of such materials as soap, silica, and aluminium chloride in conjunction with calcium chloride did not reduce permeability, but a mixture of calcium chloride and soap reduced absorption without, however, increasing strength. Soap alone increased permeability and reduced absorption and strength ; hydrated lime and soap had a similar effect. Finely-divided materials (e.g. diatomaceous earth, bentonite, etc.) reduced permeability, increased strength, and did not affect absorption. Materials such as cellulose, wax, fluosilicates, naphthalene, vaseline, and coal tar did not reduce permeability, but reduced both compressive strength and absorption. The results as a whole therefore appeared to show that such integral waterproofers as were tested were ineffective in reducing the permeability of concrete to water under pressure, although some materials reduced the rate of absorption of the specimens on simple immersion.

White and Bateman [1] report more favourably on the effect of soaps on the permeability of concrete. Comparatively few integral materials have been tested at the Building Research Station, but tests which have been made substantially confirm the general conclusion already stated.

In view of this, it is considered that certain integral waterproofers can usefully be employed to help resist the penetration of damp, but that in situations where mass concrete will be subject to a fair pressure of water reliance should not be placed primarily on the efficacy of a waterproofer to prevent percolation, but rather every means should be taken to ensure that the concrete shall have a minimum permeability. It is claimed for some products that they assist materially to this end when the conditions are those normally prevailing in practice. If so, the main factor will be that of cost ; it will be necessary to consider whether the benefit likely to accrue from the waterproofing addition will be commensurate with the extra expenditure involved, or whether the additional cost could not be expended with equal or greater advantage in improving the quality of the concrete.

The position with regard to the use of integral waterproofers in cement renderings is somewhat different from that outlined. It has already been shown that such additions to a pervious concrete may reduce the absorption under a low head, and the same applies to mortars. In renderings applied to the outside of buildings, however, the penetration of moisture is liable to occur not so much by reason of the permeability of the mass as by way of the cracks which so frequently develop as the result of shrinkage. The addition likely to be of greatest benefit, therefore, would be one which would reduce the tendency to shrinkage. No evidence is yet

[1] White and Bateman, Proc. Amer. Conc. Inst., 1926, **22**, 535.

available as to whether any waterproofers have such an effect or not. In cases where a waterproof rendering is required to be applied to a surface already damp and subject to low hydrostatic pressure, e.g. the walls of basements on wet sites, there is often considerable difficulty in making an ordinary rendering adhere. It is here that a waterproofer of the accelerator type may be of great utility. Solutions of calcium chloride (and certain other chlorides) and also of alkali silicates both possess the property of accelerating the setting of Portland cement. When used in proper concentration with neat cement or rich cement mortars, they produce setting within a few minutes, and by taking advantage of this fact a surface can be rendered with an impervious coating even against quite considerable water pressure.

One final aspect may be considered and that is that many of the specialist firms who apply proprietary waterproof renderings get very satisfactory results. This may quite possibly be due not so much to the efficacy of the waterproofer used as to the technique and skill of the operatives. Where waterproofers are employed by the ordinary builder there is a strong psychological factor involved—which may often make for success ; the operative has minute instructions on the container of the waterproofing medium, and the mixing and proportioning, as well as the preparation of the surface to be rendered, are carefully carried out.

Standard Specifications for Portland Cement.

In the tables on pp. 17 to 21 of our January number data were given from the 1928 standard specification under the heading Holland. There is now a later specification (dated 1933), and the following alterations should be made to bring the tables up to date with reference to the Dutch specification : Diameter of wire, 0.055 mm. for the 4,900-mesh sieve and 0.160 for the 900-mesh sieve ; residue, rapid hardening cement, 14 per cent. on 4,900-mesh sieve ; residue, ordinary cement, 18 per cent. on 4,900-mesh sieve ; the figure 10 mm. should be deleted in the column headed " Le Chatelier expansion " ; tensile tests should read 370 lb. for ordinary cement at 28 days and 370 lb. for rapid-hardening cement at 7 days.

Refractories which Harden by Hydraulic Action.—By W. G. Czernin. [*Tonind. Zeit.*, pp. 973/974, 987/989 (1935)]. — Excellent refractories which harden on mixing with water can be made from mixtures of aluminous cement and corundum or calcined bauxite. It is necessary to use cements low in iron, such as the German aluminous cements. The refractory can also be placed like concrete.

Masonry Cements.

"MASONRY cements" have received considerable publicity in the United States, but, as the following statement issued by the United States Bureau of Standards shows, such cements have an enormous range in composition and properties, and thus the term "masonry cement" is apparently applied indiscriminately to limes, natural cements, slag cements, and Portland cements with various additions. It is therefore to be doubted in the present stage of the exploitation of so-called masonry cements whether they have any advantage over the traditional methods of using mixtures of cement and lime made to the requirements of any particular work.

The statement is as follows:

Information on the properties of masonry cements being very meagre, or at least in general not comparable, forty-one commercial masonry cements were studied with respect to chemical composition, fineness, weight per unit volume, volumetric flow of the neat pastes, and bulk specific gravity. Mortars made from those cements were studied with respect to resistance to deformation, water-retaining capacity, volume yield, linear changes, compressive and transverse strength, durability when subjected to cycles of freezing and thawing, efflorescence, and absorption.

It was found that the cements could be classified as hydraulic limes, hydrated limes, natural cements, blast-furnace-slag cements containing various additions, several cements whose composition could not be positively determined, or Portland cements with and without admixtures the quantities of which varied from small amounts to amounts larger than the quantity of Portland cement. About half of those studied contained water-repellent additions.

The weights per cubic foot of the dry cement varied from 39.7 lb. to 89.9 lb. The amount retained on a No. 450 sieve when the cements were worked through the sieve with kerosene varied from 11.3 to 49.7 per cent. The bulk specific gravity of the neat pastes varied not only because of the different specific gravities of the cements, but because of the air emulsified during mixing. Cements containing water-repellent additions appeared to contain the most air. The bulk specific gravity of pastes gauged to an 8-in. spread in the neat spread tests varied between 0.83 and 1.93. Stirring resistance and water-retaining capacity were measured on the masonry mortars.

Cement-sand mortars of 1 : 3 by dry-rodded volumes produced from 3.3 to 4.2 volumes of mortar per volume of dry-rodded cement. The variation was caused by the variation in weight per cubic foot of the dry cement and by the amount of air incorporated during mixing.

The range in compressive strength of the mortars aged 28 days was from 50 to 3,650 lb. per sq. in. There was a sufficient relation found between modulus of rupture and compressive strength to warrant the use of the latter as a measure of the former.

The durability of the hardened specimens (1 by 4 by 6 in.) of the mortars when subjected to freezing and thawing may be predicted with reasonable

accuracy by the time required for the specimens to attain 90 per cent. of their 72-hour absorption when immersed completely in water. The rate of capillary rise when the same size specimens were placed vertically in ½ in. of water is also a gauge of the resistance to freezing and thawing. In 59 of 71 cases those mortars with a rise of 2 in. in three hours or less failed in less than 10 freezing and thawing cycles. Of those with a 2-in. rise in one hour or less all failed in 10 cycles.

Again the strength is also a gauge of resistance to freezing and thawing. For example, specimens made from a mortar (1 : 3 by volume using mixed Ottawa sand) aged 28 days in the damp closet, which failed in 10 or less cycles of freezing and thawing, had compressive strengths less than 400 lb. per sq. in. Only two having strengths less than 400 lb. per sq. in. resisted more than 100 cycles. Very few specimens failed in freezing and thawing between 10 and 300 cycles.

Efflorescence was studied by allowing the 1 in. by 4 in. by 6 in. specimens to stand on end in ½ in. of water for about one year. Maximum efflorescence developed in approximately three months. Composition of the cementing material seems to be the greatest attributive factor for efflorescence. All cements classed as natural or mixtures of Portland and natural cements effloresced. Water-repellent additions did not appear always to prevent efflorescence.

Properties of Mixtures of Portland and Aluminous Cements. By E. Rengade (*Rev. des Mat. de Constr.*, pp. 255/256, 1934).—Setting-time tests have been made with mixtures of Lafarge aluminous cement and Portland cement. The results do not agree with those obtained by Dr. K. Dorsch. It was found that except for very small admixtures of either cement in the other all the mixtures were "flash" setting. Mixtures of Lafarge aluminous cement and Portland cement are "flash" setting over a range of about 60 to 85 per cent. aluminous cement; the other proportions give mixtures which are quick setting but by no means "flash" setting. Outside the "flash"-setting range the mixtures give good strengths comparable with those of Portland cement. Mixtures of Lafarge aluminous cement and Portland cement have been used in practice and have given good results, and they have been found to be resistant to sea water. Aluminous cement concrete joins well on to Portland cement concrete. A number of existing works is described where the two types of concrete are used in contact with each other.

Cement Composition in Relation to Strength and Resistance of Mortar.

At the last meeting of the American Society for Testing Materials, Mr. H. F. Gonnerman, manager of the Research Laboratory of the American Portland Cement Association, read a paper entitled "Study of Cement Composition in Relation to Strength, Length Changes, Resistance to Sulphate Waters, and to Freezing and Thawing of Mortars and Concrete," of which the following is an abstract.

The comprehensive study of cement composition in relation to its effect on strength, length changes, resistance to sulphate waters and to freezing and thawing of mortars and concretes, inaugurated in 1930, has progressed to a point where significant results have been obtained. The tests reported here were made on 74 laboratory-prepared Portland cements covering 72 different compositions. The investigation is being continued.

The raw materials for the cements studied consisted essentially of limestone and clay, although in a number of cases flint, bauxite, iron ore or dolomite were introduced to bring the mixtures to the desired compositions. The oxide compositions of the different cement clinkers and compound compositions were computed according to the method outlined by R. H. Bogue (Industrial and Engineering Chemistry, Oct. 15, 1929). The following abbreviations are used for the several compounds: Tricalcium silicate, C_3S; beta dicalcium silicate, C_2S; tricalcium aluminate, C_3A; tetracalcium alumino ferrite, C_4AF; dicalcium ferrite, C_2F.

Reference to the strength results showed that the tensile and compressive strengths of mortar and concrete at various ages of tests are markedly influenced by the compound composition of the cement. This is to be expected when it is considered that each compound has its own characteristic strength properties and rate of gain in strength with age.

Influence of C_3S *and* C_2S.—The chief strength-giving constituents of Portland cement are the two silicates C_3S and C_2S. In the cements tested the computed C_3S content ranged from 16 to 74 per cent. by weight, and the C_2S content from 1 to 58 per cent. The sum of the two silicates ranged from 63 to 84 per cent. The present tests support the findings of others in that they indicate the predominating influence of the C_3S on the strength up to 28 days and of the C_2S on the strength beyond the 28-day period. Other conditions being the same, cements high in C_3S (and correspondingly low in C_2S) produced the highest strength at early ages. However their rate of gain in strength tends to diminish with age, so that eventually they may be surpassed in strength by cement low in C_3S (high in C_2S).

These results are based on tests from specimens exposed continuously to moisture. In considering their practical application it is important to note that even under these favourable curing conditions the cements low in C_3S gained strength slowly. Had the specimens made with such cements been given only

short periods of moist curing and then exposed to a dry atmosphere, it is probable that they would have shown considerably lower strengths than those found, particularly at the later ages. In briquette tests practically all the cements showed the typical retrogression in strength at later ages that is characteristic of this type of specimen when stored in water. Few of the cements showed any tendency toward retrogression in the compression tests of moist-cured specimens; where such a tendency occurred the cements generally contained relatively high amounts of C_3A or of C_3A plus C_4AF.

Influence of C_3A *and* C_4AF.—In a study of the effect on strength of increasing the C_3A content three groups of cements were selected, in each of which the C_3A content varied, but the C_3S, C_2S and C_4AF compounds were essentially constant, and the C_4AF varied from group to group. At ages up to 28 days both the compressive and tensile strengths increased with increase in the C_3A content, but at later ages there was in general a tendency toward lower strengths for the higher C_3A content, other conditions being the same. Results of tests on three groups of cements, each containing approximately constant amounts of C_3S, C_2S and C_3A, but variable amounts of C_4AF, indicate that the C_4AF compound produced little if any change in strength.

Influence of Individual Compounds.—Mathematical studies of the general relationships between composition and strength were made in order to derive equations that would give reasonably good agreement between calculated and observed values. It was found that linear equations of the form

$$a\,C_3S + b\,C_2S + c\,C_3A + d\,C_4AF = \text{strength}$$

served the purpose. The coefficients in these equations and their probable errors were computed by the method of least squares. For all types of specimens the C_3S is continuously effective in increasing strength. The C_2S contributes little strength up to about 28 days but is largely responsible for the increases in strength beyond that period.

After the 7- and 28-day periods for 1 : 4.25 and 1 : 2.75 cubes in compression and at all ages up to 28 days for 1 : 3 briquettes in tension, the C_3A appears to exert a greater effect on the strength than any of the other constituents. Its effect on strength diminishes beyond the 28-day period, and at one and two years it is either nearly zero or negative. In the case of concrete cylinders the decrease in the effectiveness of the C_3A after the 28-day period was found to be less rapid. The C_4AF had a negative effect on the compressive strength of 1 : 2.75 cubes up to about 7 days, and in the case of the 1 : 4.25 cubes its effect was slight at all stages. In the case of the briquettes the C_4AF appears to add to the tensile strength after one day, although its effect diminishes beyond the three-month period.

The high values of the C_3A factors at 28 days are not easily explained. Bogue and Lerch consider the effect to be due to a secondary cause rather than to a direct contribution to strength of the order indicated. They suggest that since C_3A requires a larger amount of water for hydration than the other cement compounds, increasing its percentage in a series of tests such as this, where a nearly uniform quantity of water is used for mixing, will increase the amount of water

that will be taken up by the C_3A, leaving decreasing amounts for the silicates. The resulting decreased water-silicates ratio may then result in improved strength commonly associated with decreased water-cement ratios. Bogue and Lerch further suggest that the negative values of the factors for C_4AF may be due to a deposition of colloidal hydrated $CaO.Fe_2O_3$ around the grains of the other compounds, thus delaying their rate of reaction with water.

Cement Composition and Length Changes.

For studying the influence of cement composition on length changes, 3 by 3 by 15-in. mortar bars of 1 : 3.6 mix by weight were used. Expansion and contraction were found to be virtually independent of the relative proportions of C_3S, C_2S and C_4AF, but variations in the proportion of C_3A had an appreciable influence. In general, as the C_3A content increased there was a tendency toward increased expansion of the bars during three months' storage in the moist room, and increased total contraction after fourteen months' and two years' storage for bars allowed to dry in the air of the laboratory at about 50 per cent. relative humidity. The tests include both seven days' and three-months' storage in a moist room before drying.

For the bars moist-cured for seven days, the values of total contraction at fourteen months ranged from 0.07 per cent. for a C_3A content of zero to about 0.11 per cent. for a C_3A content of 20 per cent. Approximately the same range in total contraction was obtained at an age of two years for the bars that were moist-cured for three months before they were allowed to become dried out in the air of the laboratory.

Composition and Total Contraction.—Coefficients of linear equations representing the relation between composition and total contraction of the mortar bars were derived by the method of least squares, using those cements that contained less than 1 per cent. free lime and approximately 3 per cent. MgO. An analysis in the laboratory of 57 cements showed the following coefficients and probable errors for the different compounds :—

COEFFICIENTS OF LINEAR EQUATIONS.

Compound.	After 7 days' moist curing. Total age 12 months.	After 3 months' moist curing. Total age 15 months.
C_3S	0.00079 ± 0.000036	0.00082 ± 0.000036
C_2S	0.00077 ± 0.000033	0.00077 ± 0.000035
C_3A	0.00234 ± 0.000100	0.00213 ± 0.000105
C_4AF	0.00049 ± 0.000114	0.00046 ± 0.000118

The two silicates appear to have influenced total contraction to approximately the same degree but to a much less degree than the C_3A, and to a somewhat greater degree than the C_4AF. Other investigators have also reported that the C_3A compound has the greatest influence on the total contraction of mortar bars.

TABLE I.

MAXIMUM C_3A CONTENTS FOR RESISTANCE TO SULPHATE SOLUTIONS.

Type of Specimen.	Water-Cement Ratio by Weight.	Maximum C_3A Content for Good Sulphate Resistance at Period Indicated.					
		2 per cent. $MgSO_4$ Solution.			2 per cent. Na_2SO_4 Solution.		
		1 yr.	2 yr.	3 yr.	1 yr.	2 yr.	3 yr.
3-in. by 6-in. concrete cylinders ..	0.563	10	8	7	12	11	10
1 : 2.75 mortar cubes	0.533	8	7	6	9	8	6
1 : 4.25 mortar cubes	0.800	8	8	7	8	7	6
1 : 3 briquettes	0.400	9	8	6	12	10	9

Cement Composition and Resistance to Sulphate Solutions.

Concrete cylinders, 2-in. plastic mortar cubes, and standard briquettes made with each cement were, after 28 days of moist curing, stored in tanks containing 2 per cent. solutions of magnesium and sodium sulphate.

Detrimental Effect of C_3A.—The data on the resistance of the cements to the sulphate solutions as influenced by each of the four major compounds were studied in the same manner as that employed in studying strength and length changes. No significant trends were observed for any of the compounds except C_3A. These studies as well as analyses of the durability factors showed that the C_3A had a marked detrimental influence on the sulphate resistance of the cement. It is of particular interest to note that lean 1 : 4.25 cubes made with cement low in C_3A showed much better performance than the richer 1 : 2.75 cubes made with cements high in C_3A. This confirms the findings of Bogue and Lerch that certain changes in composition have a greater effect upon resistance to sulphate attack than changes in richness of mix and water-cement ratio.

The maximum C_3A contents for good resistance to the solutions were determined for each type of specimen. The values are shown in Table I. It is seen from these values for the three-year period that good resistance to magnesium sulphate solution was obtained with all types of specimens when the C_3A content did not exceed 6 or 7 per cent., and in the case of the sodium sulphate solution when it did not exceed 6 to 10 per cent.

Strength in Sulphate Solutions.—The strengths of specimens stored in sulphate solutions were expressed as a percentage of the strength of similar specimens stored in water and tested at the same age. The values obtained were, at corresponding ages, in fair agreement with the maximum C_3A contents for good sulphate resistance, discussed in the preceding section, which were derived from the durability factors.

Expansion in Sulphate Solutions.—The linear expansions of 3-in. by 6-in. concrete cylinders made from 38 of the cements were measured at various periods of storage in 2 per cent. solutions of sodium and magnesium sulphate and in water after 1 day in the mould and 27 days in the moist room. The expansions of the cylinders in the solutions conformed closely to those of the cylinders in

water until the action of the sulphate caused a sharp increase in the rate of expansion that marks the beginning of visual disintegration. In general, as the expansion increases, the extent of disintegration also increases. Where the C_3A content is 7 per cent. or less the expansions up to the two-year period were not excessive except in the case of a cement that contained 2.3 per cent. uncombined lime. Expansions in water also tended to decrease with C_3A content.

Freezing and Thawing.

Specimens used for freezing and thawing tests consisted of three 3-in. by 6-in. concrete cylinders for each of 66 of the cements. These cylinders had been moist-cured for 28 days and then stored in the air of the laboratory at approximately 50 per cent. relative humidity for periods of 12 to 27 months. A special procedure was employed, involving twelve cycles of freezing and thawing, a 72-hour drying and 72-hour saturation period, plus the time for cooling and measuring, requiring in all two weeks.

Numerous studies were made of individual groups of cements, to see if there was any variation in their resistance to alternate freezing and thawing due to variation in composition. These studies indicated a trend toward increased resistance with increase in the C_3S and C_2S compounds, and a trend toward decreased resistance with increase in the C_3A and C_4AF compounds, the latter compound having considerably less effect than C_3A.

In a group of twelve cements the composition was varied in two ways by varying the MgO content. In six of the cements MgO was substituted for CaO in the raw mix, causing the C_3S to decrease from 49 to 11 per cent. and the C_2S content to increase from 29 to 58 per cent., while the C_3A and C_4AF remained substantially constant at 11 and 10 per cent. respectively. The MgO content of these six cements varied from 1.2 to 9.7 per cent. In the other six cements investigated, the MgO was used as an addition to the raw mix. When it was introduced, adjustments were made in the CaO and SiO_2 to maintain the C_3S approximately constant at 45 per cent. The C_2S decreased from 36 to 23 per cent., and the C_3A and C_4AF remained constant at 11 and 9 per cent. respectively. The MgO in these cements varied from 1.4 to 9.9 per cent.

Results with MgO Cements.

Substitution of MgO for CaO in the raw mix produced cement which showed at all ages a gradual decrease in strength with an increase in MgO content, apparently due to a change in the relative proportions of C_3S and C_2S. The addition of MgO in the raw mix produced little effect on the strength of either mortar or concrete except for an MgO content of 7 per cent. or more where decreased strength occurred at the one and two-year periods.

Concrete cylinders stored in water for 20 months showed increased expansion with increase in the MgO content of the cement regardless of whether MgO was added to the raw mix or substituted for CaO.

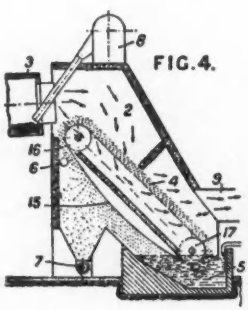
Excessive expansion in sulphate solutions was recorded where the MgO content was greater than 5 or 6 per cent. in the case of magnesium sulphate and when greater than 7 per cent. in the case of sodium sulphate. Concrete subjected to alternate freezing and thawing showed a tendency toward increased expansion and greater loss in weight as the MgO content of the cement increased.

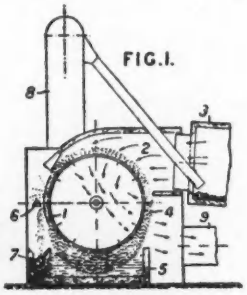
Recent Patents Relating to Cement.

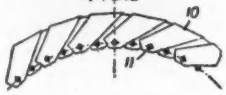
Cements.

416,082. Fasting, J. S., 33, Vestergade, Copenhagen. March 9, 1933.

In apparatus for the manufacture of cement of the kind in which the raw slurry before delivery to a rotary kiln (3) is dried and preheated by the waste gases from the kiln, the slurry is applied as a film to the surfaces of carrier bodies, *e.g.*, pieces of chain or netting, attached to a movable support at points which move in a closed path of such form that, during part of their travel, the bodies form a layer resting on the support, and while in this position are subjected to the action of the hot gases. Fig. 1 shows chains (4) attached to the outer surface of a rotary perforated drum (1) disposed within a chamber (2) fitted with a slurry tank (5) into which the chains dip and which is traversed by the gases on their way from the kiln (3) to the outlet (9).







The dried material is removed from the chains by a rotary beater (6) and is delivered to the kiln by a worm (7) and elevator (8). A modification is described in which chains are attached to both the inner and outer surfaces of the drum (1). Fig. 4 shows a further construction in which the drum (1) is replaced by an endless perforated band (15) running over sprockets (16, 17). The employment of worm (7) and elevator (8) may be rendered unnecessary by arranging the preheater at a level above that of the upper end of the kiln, a chute being provided to convey the dried slurry directly into the kiln. The chains (4) may be replaced by pieces of sheet iron (10, Fig. 2), pivotally mounted on bars (11) which form part of the supporting structure.

Cements.

409,120. Case, G. O., Cothill, Chipstead, Sevenoaks, Kent, and Carbo-Lime & Cement Co., Ltd., Sentinel House, Southampton Row, London. March 14, 1933.

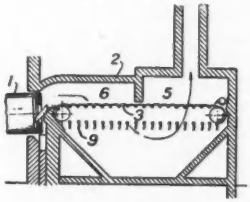
Hydraulic cement is made by mixing and grinding together a finely ground clinker material containing tricalcium silicate, *e.g.*, Portland cement, and carbonate of lime which has been artificially dried and contains less than 0.5 per cent. of moisture. The carbonate is preferably ground to pass an 8-mesh sieve and so to be relatively coarse compared with the clinker. The proportion of dry carbonate is preferably 8 parts of carbonate to 1 of free calcium oxide in the

clinker. In an example limestone or other calcium carbonate is crushed to pass a one-inch mesh, dried so that not more than 0.5 per cent. of moisture remains, and ground to pass an 8-mesh sieve. The ground dry carbonate is then mixed with clinker of a fineness to have not more than 1 per cent. residue on a 76-mesh sieve and not more than 10 per cent. on a 180-mesh sieve. The mixture is then ground until the whole passes through a 50-mesh sieve.

Cement

407,941. Nielsen, N., 44, Fuglebakkevej, Frederiksberg, near Copenhagen. September 24, 1932.

In the manufacture of cement by the wet process, the raw slurry material is, without being nodulised, formed into a coherent layer on a gas-permeable bed. For this purpose it is subjected to a preliminary heating process sufficient to cause it to become porous as a result of the formation of cracks and pores. Hot gases are then passed through the layer which is thereafter fed, without further grinding, into a kiln. A mechanical device such as a spiked roller may be used to assist the formation of pores and cracks. When the slurry is applied to the bed in liquid form the preliminary heating may be effected by passing hot gases upwards through the bed so that they bubble through the layer of slurry. Alternatively the hot gases may be led along the



surface of the slurry while the openings in the bed are kept shut by dampers or the like. In this case the slurry may be partially dewatered, or stiffened by the addition of dry material. The gas-permeable bed is preferably movable and may consist of a chain grate, a rotating perforated table, or a cylinder of metal which may be made of a heat-resisting alloy or covered with perforated refractory material. The hot gases are arranged to pass first through the material and then through the bed so that the bed is not exposed to extremely hot gases. The same hot gases can be used subsequently for the preliminary drying. In the arrangement shown, a kiln smoke chamber (2) at the inlet end of a rotary kiln (1) contains a grate formed by an endless band (3) having hinged flaps (9) adapted to swing into the vertical position when they reach their lower position. The smoke chamber above the grate is divided into two chambers (5, 6) in the first of which the slurry material on the grate is dried and in the second of which the material is subsequently further heated.

Flame Furnace for Burning Cement
(BRITISH PATENT NO. 409139)
The proprietor desires to introduce his invention under licence or otherwise.
Send for particulars to :—
Dr. KYRIACOU
5, AVENUE FRANKLIN, ST. GERMAIN-EN-LAYE, FRANCE.

Refractory Substances.

409,130. Seil, G. E., Conshohocken, Pennsylvania, U.S.A. April 10, 1933.

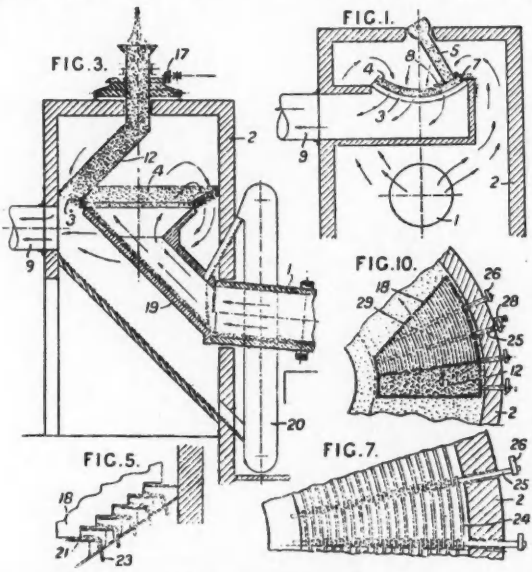
A chromite refractory material in which low melting point gangue has been converted into refractory material is prepared by intimately mixing chrome ore and dead burnt crystallised magnesium oxide, the magnesium oxide being greater than 12½ per cent. and preferably between 17 and 25 per cent. of the mixture and sufficient or slightly more than sufficient to convert the gangue, grinding and tempering the mixture and shaping and turning the mass preferably at about 3,000 deg. F. The chrome ore is heat treated at a temperature at least equal to that of the final burning together with all or part or without any of the magnesium oxide, the remainder being added prior to tempering. The low melting constituent of the chrome ore is by the treatment converted into the material known as forsherite.

Cement Manufacture.

414,118. Middelboe, K., 14, Thorvaldsensvej, Frederiksberg, near Copenhagen. January 30, 1933.

In apparatus for the manufacture of cement in which the waste gases from a rotary kiln (1) are utilised in a chamber (2) for preheating the raw charge material, the preheater is provided with a fixed gas-permeable support (3) on which a layer (4) of material is maintained stationary during the passage of the heating gases. In the form shown in Fig. 1, the support (3) comprises curved bars on to which a layer of material is delivered by a swinging chute (5) fitted with pivoted scrapers (7, 8) of which, during each swing, the one on the leading edge serves to discharge the layer deposited during the preceding swing and preheated to the desired degree by the passage of the waste gases from the kiln (1) to the outlet (9). Fig. 3 shows a construction in which the support (3) is in the form of an annular stepped grate, the charging

and discharging device being constituted by a rotary chute (12) carrying a scraper (18, Fig. 5) and operated by gearing (17). The treated material discharged by the scraper (18) reaches the kiln through a chute (19) into which are also delivered, by an elevator (20), the riddlings which fall through the grate. The scraper (18) carries short chains



CEMENT MANUFACTURE.

(23, Fig. 5), which extend through the gaps between the grate members (21) and prevent obstruction thereof. In a further modification, Figs. 7 and 10, the annular grate is formed of movable sectors each comprising short bars (24) mounted on a rocking-shaft (25), the chute (12) and scraper (18) being spaced apart a distance (29, Fig. 10) greater than the length of a grate sector. This arrangement leaves each sector in succession free of charge material, and during this free interval the sector is rocked to free the bars from any jammed material by the engagement of a roller (28), mounted on the chute (12), with an arm (26) projecting from the shaft (25).

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